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Refinement of the structure of CuV_2O_6.

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CuV_2O_6 is triclinic, $C\bar{1}$ (an unconventional setting of $P\bar{1}$), with $a=9{\cdot}168$ (5), $b=3{\cdot}543$ (3), $c=6{\cdot}478$ (7) Å, $\alpha=92{\cdot}25$ (8), $\beta=110{\cdot}34$ (7), $\gamma=91{\cdot}88$ (6)°, $\varrho_{calc}=4{\cdot}35$, $\varrho_x=4{\cdot}30$ g cm^{-3}. Crystals were grown in an oxygen atmosphere from a melt whose composition corresponded to 0·50 mole % CuO and V_2O_5. The structure is closely related to that of the mineral brannerite, $ThTi_2O_6$ [Ruh, R. & Wadsley, A. D. (1966). *Acta Cryst.* **21**, 974–976] with the symmetry reduced from $C2/m$ because of a Jahn–Teller distortion of the CuO_6 octahedra. The VO_6 octahedra is also distorted with the vanadium ion displaced from the center towards an edge of the polyhedron.

Introduction

The intensities and cell dimensions were obtained from a crystal with average linear dimension of 0·1 mm utilizing a Syntex $P\bar{1}$ automatic diffractometer (Mo $K\alpha$, $\lambda=0{\cdot}71069$ Å, graphite-monochromated, θ–2θ scan, scintillation counter with pulse-height discrimination, one check reflexion measured every fifty with backgrounds measured 1° on either side of the peak). 1163 symmetry independent reflexions had a positive intensity, with 1060 above 3σ. Absorption corrections were applied. The systematic absences were hkl with $h+k$ odd. Trial parameters were taken from those reported by Lavaud & Galy (1972) for CuV_2O_6 with apparent $C2$ symmetry, with the Cu ion placed at the center of symmetry at the origin. Full-matrix least-squares refinement with anisotropic thermal parameters and weights chosen so that $\omega(|F_o|-|F_c|)^2$ would be independent of F_o yielded a final R value of 0·047, unobserved reflexions with F_c greater than 3σ included. The final atomic parameters are in Tables 1 and 2. The bond lengths and angles are in Table 3. Observed and calculated structure factors are in Table 4.

Table 1. *Atomic parameters for* CuV_2O_6 *with standard errors in parentheses*

	x	y	z
Cu	0	0	0
V	0·19279 (4)	0·01267 (10)	0·65463 (6)
O(1)	0·0304 (2)	0·0027 (5)	0·7239 (3)
O(2)	0·3426 (2)	0·0482 (6)	0·8896 (3)
O(3)	0·3067 (2)	−0·0028 (5)	0·4316 (3)

Discussion

CuV_2O_6 is one of a series of MV_2O_6 compounds showing nearly identical structures. Some of these, such as ZnV_2O_6

Table 2. *Thermal parameters* ($\times 10^4$) *for* CuV_2O_6 *with standard errors in parentheses*

The $U_{ij}=2\pi^2 b_i b_j \beta_{ij}$ where the β_{ij} appear in the structure-factor expression as exp $-[h^2\beta_{11}+2hk\beta_{12}+\ldots]$ and the b_i's are reciprocal lattice vectors.

	U_{11} (Å)^2	U_{22} (Å)^2	U_{33} (Å)^2	U_{12} (Å)^2	U_{13} (Å)^2	U_{23} (Å)^2
Cu	97 (2)	103 (2)	67 (2)	0	60 (2)	0
V	64 (2)	42 (2)	51 (2)	15 (1)	46 (1)	5 (1)
O(1)	95 (7)	95 (6)	97 (7)	−0 (5)	79 (5)	−6 (5)
O(2)	103 (7)	114 (7)	79 (7)	7 (5)	38 (5)	7 (5)
O(3)	94 (7)	46 (5)	91 (7)	21 (4)	67 (5)	11 (5)

Table 3. *Interatomic distances and angles in* CuV_2O_6 *with standard errors in parentheses*

Cu–O(1)a, b	1·904 (2) Å	O(1)a–Cu–O(2)c	90·9 (1)°
Cu–O(2)c, d	2·049 (2)	O(1)a–Cu–O(2)c'	87·7 (1)
Cu–O(2)c', d'	2·438 (2)	O(2)c–Cu–O(2)c'	104·0 (1)
V–O(1)b	2·588 (2)	O(1)b–V–O(3)a	76·3 (1)
V–O(3)a	2·056 (2)	O(1)b–V–O(1)a	77·0 (1)
V–O(1)a	1·697 (2)	O(1)b–V–O(2)a	175·6 (1)
V–O(2)a	1·655 (2)	O(1)b–V–O(3)d	80·9 (1)
V–O(3)d	1·871 (2)	O(1)b–V–O(3)d'	76·0 (1)
V–O(3)d'	1·845 (2)	O(3)a–V–O(1)a	153·2 (1)
		O(3)a–V–O(2)a	100·6 (1)
		O(3)a–V–O(3)d	73·8 (1)
		O(3)a–V–O(3)d'	75·4 (1)
		O(1)a–V–O(2)a	106·2 (1)
		O(1)a–V–O(3)d	99·8 (1)
		O(1)a–V–O(3)d'	100·2 (1)
		O(2)a–V–O(3)d	101·5 (1)
		O(2)a–V–O(3)d'	100·2 (1)
		O(3)d–V–O(3)d'	144·9 (1)

Symmetry transforms (except for translations by a unit cell length)

$a=x,y,z$; $b=-x,-y,-z$; $c=\frac{1}{2}+x,\frac{1}{2}+y,z$; $d=\frac{1}{2}-x,\frac{1}{2}-y,-z$.

Table 4. *Observed and calculated structure factors for* CuV_2O_6

(Angenault & Rimsky, 1968) and CuV_2O_6 (Lavaud & Galy, 1972), have been refined in space group $C2$ and others such as β-CdV_2O_6 (Bouloux & Galy, 1969), MgV_2O_6 (Ng & Calvo, 1972) and CoV_2O_6 (Sauerbrei, 1972) in space group $C2/m$. CaV_2O_6 and α-CdV_2O_6 (Bouloux, Perez & Galy, 1972) have a slightly different structure as a result of a lost weak sixth V–O interaction.

The structure of CuV_2O_6 is derived from a hexagonally pseudo close-packed arrangement of oxygen atoms with both Cu and V atoms octahedrally coordinated and with (101) as the stacking direction as shown in Fig. 1. Although the Cu ion lies in an ordinary octahedral site, albeit distorted, in the close packed array of oxygen atoms the V ion actually lies in a distorted tetrahedral site formed with

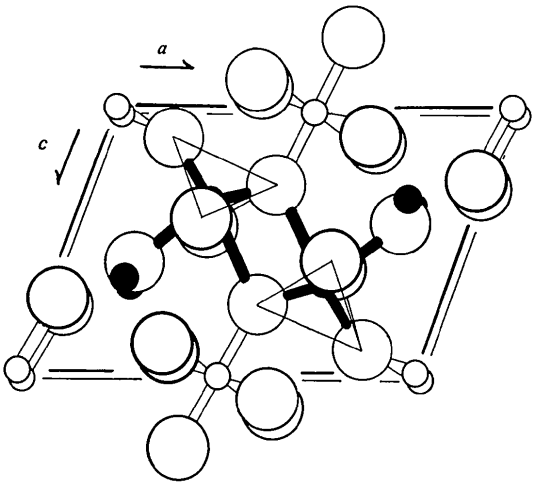

Fig. 1. Structure of CuV_2O_6 projected normal to the *ac* plane. The small open circles are Cu atoms and the filled circles are vanadium atoms. The larger circles are oxygen atoms. The filled bonds indicate the V–O bonds of the VO_6 groups with V at $y=\frac{1}{2}$. The pseudo-tetrahedral group is outlined.

O(1) in one layer and O(2), O(3) and O(3)*d'* in an adjacent layer. These four atoms lie between 1·655 and 1·871 Å from the vanadium ion. The O(3)–V–O(3)*d'* bond angle is enlarged to 144·9° in order to accommodate a fourth oxygen atom in the same layer and the sixth V–O bond length involves an interaction to a third layer of oxygen atoms. These latter bond lengths are 2·056 (2) Å for V–O(3)*a* and 2·588 Å for V–O(1)*b*.

Each CuO_6 group shares two edges with CuO_6 groups displaced by a *b*-axis translation. The tetrahedral part of the VO_6 group share corners, forming chains running parallel to **b**, with adjacent chains sharing oxygen atoms to generate VO_5 groups. These double chains share an additional oxygen atom with adjacent double chains, yielding the distorted VO_6 groups.

The elongated Cu–O(2)*c'*, *d'* bonds, presumably arising from a Jahn–Teller distortion, destroy the mirror plane of the space group *C*2/*m* of the nearly isotypic MgV_2O_6 structure (Ng & Calvo, 1972) while the Cu–O(1)*a* and –O(1)*b* bonds contract to 1·904 Å in order to maintain the bond strength about the Cu^{2+}. If these latter bonds were to elongate, the *C*2/*m* space group could be maintained but with serious underbonding at these oxygen atoms since they are linked strongly to only one vanadium and weakly to a second.

The structural results obtained by Lavaud & Galy (1972) on CuV_2O_6 might suggest a phase transformation from the present structure to a monoclinic form with a disorder among Cu–O(2) leading to the reported bond length of 2·26 Å. A differential thermal analysis showed no evidence of such a transformation however. Further, the present results are consistent with the bond-strength–bond-length correlations proposed by Brown & Shannon (1973) as discussed for the other cupric vanadates in this series by Shannon & Calvo (1973).

The results of this analysis are shown in Table 5 where the bond strengths are determined from $S_{Cu^{2+}} = \frac{1}{3}(2{\cdot}084/R)^{5{\cdot}3}$ and $S_{V^{5+}} = \frac{5}{4}(1{\cdot}714/R)^{5{\cdot}1}$ where R is the appropriate bond length. Note that the empirically determined constants were derived for V^{5+} in a variety of coordinations.

Table 5. *Emperical bond strengths in* CuV_2O_6

	From Lauvaud & Galy		Present result	
Bond	Bond length (Å)	Bond strength	Bond length	Bond strength
Cu–O(1)	1·92 2×	0·51 2×	1·904 2×	0·542 2×
Cu–O(2)	2·26 2×	0·22 2×	2·049 2×	0·370 2×
Cu–O(2)′	2·29 2×	*0·20* 2×	2·438 2×	*0·148* 2×
		∑1·86		∑2·12
V–O(1)*b*	2·57	0·16	2·588	0·155
V–O(3)*a*	2·08	0·47	2·056	0·501
V–O(1)*a*	1·70	1·30	1·697	1·310
V–O(2)*a*	1·63	1·78	1·655	1·494
V–O(3)*d*	1·97	0·61	1·871	0·799
V–O(3)*d'*	1·73	*1·19*	1·845	*0·866*
		∑5·51		∑5·12

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